



New Bases for Coating and Plastic Compositions*

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In searching the literature for information on polyallyl ethers and carbohydrates, it is possible to find a few scattered references; however, it is apparent that in most cases the methods of preparation and characterization of the resulting compounds leave much to be desired. Furthermore, to the best of our knowledge, the interesting properties of these materials, especially their ability to polymerize in the presence of oxygen, had not been recognized. Recently in this laboratory a study was made of several allyl ethers of polyhydric alcohols, including starch, ethylene glycol, glycerol, alpha-methyl glucoside, D-mannitol, D-sorbitol, inositol, dipropylene glycol, 1,3-butylene glycol, pentaerythritol, and sucrose. The object of this paper is to present our results on the methods of preparation and the determination of properties of the above ethers; their possible utilization as coatings, adhesives, and plastic intermediates will also be discussed. Owing to the complexity of starch, its allyl ether differs considerably in physical properties from those of simple carbohydrates. For this reason it will be treated separately and somewhat more in detail.

Allyl Ether of Starch

The only reference to allyl starch in the literature is that in Tomecko and Adams (J. Am. Chem. Soc., 45, 2698, 1923), who prepared what they called a mono-allyl starch by direct substitution of starch with allyl bromide in the presence of 10 per cent. aqueous potassium hydroxide. The product had 0.5 allyl group per glucose unit. Repetition of the experiments of Tomecko and Adams gave a white amorphous powder, slightly soluble in water and practically insoluble in acetone, ethylene chlorohydrin, and other organic solvents, with 0.5 allyl group per glucose unit. This

was similar to the substance obtained by Tomecko and Adams. They determined the degree of substitution by combustion analyses. We used the same method for insoluble compounds and Wijs' method for compounds soluble in organic solvents. Slight modifications in the concentrations of starch, alkali, or allyl bromide or in the reaction time did not affect the composition of the final product.

A clue to the explanation of low substitution in the product obtained by Tomecko and Adams was found in the fact that no allyl bromide could be recovered in spite of the large excess (85 g. to 10 g. starch or a mole ratio of 11.1). This was attributed to two side reactions, which parallel the main reaction of etherifying the hydroxyl groups of the starch. The allyl bromide is hydrolyzed by the alkali to allyl alcohol, and this reacts with allyl bromide, forming allyl ether. The hydrolysis of allyl bromide and also of allyl chloride (used in later experiments) at various temperatures and with various concentrations of alkali was therefore investigated. Equal volumes of allyl bromide or chloride and sodium hydroxide solution were mixed and stirred at various temperatures for three hours. At 80° C. (approximately the temperature of the reaction for the preparation of allyl starch) the results were as follows: With alkali concentrations up to 10 per cent., about 23 per cent. of allyl bromide was hydrolyzed; with 20 to 30 per cent. alkali, about 9 per cent.; and with 40 to 50 per cent., only about 2.5 per cent. About 21 per cent. allyl chloride was hydrolyzed with 10 per cent. NaOH, and only about 1 per cent. with 40 to 50 per cent. alkali.

These experiments pointed to the advisability of using higher concentrations of alkali in the preparation of allyl starch. As a matter of fact, when concentrated alkaline solutions were used, with the same excess of allyl bromide, compounds of a higher degree of substitution (up to .6 allyl groups per glucose molecule) were obtained, and considerable allyl bromide could be recovered after the reaction was complete. The powdery product thus obtained was infusible and insoluble in all organic solvents tested.

Various Methods of Preparation of Allyl Starch

On the assumption that easily oxidizable allyl starch might be more stable in solution, we adopted a method similar to that used by Haworth, Hirst, and Webb (J. Chem. Soc., 1928, p. 268) for methylation of starch, that is, simultaneous hydrolysis and allylation of starch acetate in acetone solution. This method, which does not require an autoclave, is carried out as follows: In a flask fitted with a mechanical stirrer and reflux condenser, 100 g. of starch acetate is dissolved in 250 cc. of acetone; 250 g. of 50 per cent. aqueous NaOH and 300 cc. of allyl bromide are added; and the mixture is heated at reflux temperature for 3½ hours. The volatile portion of the reaction mixture is then removed rapidly (15 min.) by distillation with steam, and the gummy product remaining in the flask is washed until alkali-free.

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Material used	% moisture	Reaction time, hrs.	Yield, gms.	Yield corrected for moisture of the product	Yield, % of theoretical	Allyl content (Wijs' method)	Allyl groups per glu- cose unit	Allyl chloride recovered, gms.	Allyl ether recovered, gms.
Potato starch	16	11	860	612	93	37.0	2.3	795	94
Potato starch	16	11	890	620	94	37.1	2.3	1213	79
Sweet potato starch	14	10	900	603	99	30.0	1.7	924	117
Cornstarch	12	10	986	684	98	37.4	2.4	770	72
Cornstarch	12	10	972	676	96	37.6	2.4	682	106
Tapioca starch	13	9	830	617	92	35.0	2.1	823	93
Waxy-maize starch	10	20	900	617	92	33.5	2.0	460	68
Standard tapioca dextrin (viscosity 8.5 centistokes in 50% sol. at 130° F.)	3	4	816	646	89	33.2	2.0	1222	89

*Based on a paper read before the meeting of Paint and Varnish Production Clubs New York City, on October 24, 1944, and on the articles published by Nichols and Yanovsky in J. Am. Chem. Soc., 66, 1625 (1944); 67, 46 (1945), and by Nichols, Hamilton, Smith and Yanovsky in Ind. Eng. Chem., 37, 201 (1945).

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after which it is dissolved in about 150 cc. of acetone. When this acetone solution is poured into rapidly stirred water at room temperature, nearly white gummy allyl starch is obtained. The yield is about 90 g. of the gum, containing about 20 per cent. of water. An appreciable portion of the allyl bromide can be recovered from the steam-distilled liquid.

The same compound can be prepared with allyl chloride, which is cheaper. But for this reaction heating in an autoclave at 86° C. for about 11 hours is required.

For producing larger quantities of allyl starch, the following method is more economical. Five hundred grams of air-dry starch is stirred into 2000 g. of 50 per cent. aqueous NaOH in an autoclave at room temperature, and 2500 cc. of acetone and 3000 g. of allyl chloride are added, with constant stirring. The autoclave is heated at about 86° C. (approx. 10 pounds pressure). The liquid is then distilled with steam for about 40 minutes. The separated gum is washed free of alkali and excess of allyl chloride. Acetone, allyl chloride, and allyl ether can be recovered from the distillate. The results of several runs are given in Table I. They were obtained with the laboratory equipment available and do not represent the optimum yields and recovery of solvent. This table shows that for most ordinary starches the reaction time is about 10 hours; for waxy-maize starch, which consists entirely of amylopectin, it is 20 hours; and for a starch degradation product like dextrin it is 4 hours. The per cent. of allyl in the product decreases somewhat with time, owing to the slow oxidation and polymerization of allyl starch, even at room temperature or below. The yields are given on a wet basis (20-25 per cent. moisture).

No attempt was made to recover the acetone from the steam distillate, which was washed with water and then fractionated to recover the allyl chloride and allyl ether. Perhaps in commercial practice the mixture of allyl chloride and acetone could be used for making the next batch.

Physical and Chemical Properties of Allyl Starch

Allyl starch prepared by these methods is a soft, gummy (but not tacky) material containing about 2 allyl groups per glucose unit. Products of lower or higher allyl content can be obtained, but they are either powdery or extremely sticky. The powdery form, due to a large surface exposed, is much less stable. The gummy allyl starch, when left in the air, becomes coated with a hard insoluble material, but this can be avoided by keeping the allyl starch under water at a comparatively low temperature. It is soluble in most organic solvents but not in aliphatic hydrocarbons. Solutions of allyl starch in acetone, alcohol, and other solvents are stable. Even a 30 per cent. solution has low viscosity. One of the methods for the purification of allyl starch is precipitation from alcohol or acetone solutions with water.

TABLE II

Insolubilization of Allyl Starch Films
With and Without Cobalt Naphthenate

Drier, % Co	Temp., °C.	Type of heating	Percent insoluble material after time, in hours, indicated							
			1	2	3	4	5	6	24	
---	120	Oven	---	100	---	---	---	---	---	
0.4	120	...	---	100	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Infrared	---	97	---	---	---	---	---	
0.2	120	...	---	97	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Infrared	---	98	---	---	---	---	---	
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0.4	120	Oven	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Infrared	---	98	---	---	---	---	---	
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0.4	120	Oven	---	98	---	---	---	---	---	
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0.4	120	Oven	---	98	---	---	---	---	---	
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0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
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0.4	120	Infrared	---	98	---	---	---	---	---	
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0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
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0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
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0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
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0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Oven	---	98	---	---	---	---	---	
0.2	120	...	---	98	---	---	---	---	---	
0.4	120	Infrared	---	98	---	---	---	---	---	
0.2	120	...	---</							

ingly, polyallyl ethers of alpha-methyl glucoside, sucrose, mannitol, sorbitol, inositol, pentaerythritol, glycerol, ethylene glycol, 1,3-butylene glycol, and dipropylene glycol were prepared.

The following general laboratory method was used for the preparation of the allyl ethers of polyhydroxy compounds. One equivalent of the polyhydric alcohol was suspended in 2 equivalents plus a 10 per cent. excess of 50 per cent. aqueous sodium hydroxide in a 3-neck flask equipped with condenser, dropping funnel, and stirrer. The equivalents of allyl bromide were added dropwise to the well-stirred reaction mixture over a period of 4 to 6 hours; the temperature was maintained at 70 to 75°. The reaction was allowed to proceed for an additional hour; then the product was extracted with ether, washed free of alkali, and distilled. The higher boiling allyl ethers, such as those from sucrose, sorbitol, and inositol, were distilled with steam before final distillation in vacuum. In most cases this method gave compounds with an allyl content of 75 to 100 per cent. of the theoretical value.

Complete allylation of these compounds is described by Nichols and Yanovsky (J. Am. Chem. Soc., 66, 1625, 1944; 67, 46, 1945).

All the polyallyl ethers of the compounds prepared by this method were liquids which could be purified by distillation in *vacuo*, giving clear and colorless compounds. Their properties are summarized in Table IV.

In the presence of air or oxygen, these compounds slowly polymerized, first to more viscous liquids and finally to transparent resins. This process was catalyzed by heat and various paint driers.

The changes in viscosity occurring during the polymerization of tetra-allyl alpha-methyl glucoside are shown in Table V. The gradual increase in viscosity, followed by a marked increase to the point of gelation, along with the insoluble and infusible nature of the final product, is characteristic of the formation of a three-dimensional network. Figure I shows the change in viscosity of allyl-alpha-methyl glucoside (3.5 allyl groups) under various con-

TABLE IV
Properties of Allyl Ethers of Polyhydroxy Compounds

Compound	Boiling point, at 1 mm., °C.	Refractive index n_D^{20}	Density, d_4^{20}	Molecular refraction		Viscosity at 25° C., centipoises	Specific rotation, $[\alpha]_D^{25}$ (8% sol. in abs. alcohol)	Percent allyl	
				Calc.	Found			Calc.	Found
Tetraallyl alpha-methyl glucoside	160-162*	1.4710	1.0345	95.73	95.76		115.6°	46.4	45.95
Triallyl glycerol	82-83	1.4510	0.9362	61.16	61.05	2.02	--	58.0	57.1
Hexaallyl mannitol	170-172	1.4710	0.9866	120.09	119.70	14.52	14.0°	58.3	57.5
Hexaallyl sorbitol	163-165	1.4704	0.9837	120.09	119.93	12.67	8.56°	58.3	57.4
Heptaallyl sucrose	-	1.4912	1.1071	164.79	163.01	792.5	50.5°	46.2	44.3
Hexaallyl inositol	169-170	1.4788	1.0115	117.89	117.85	22.52	--	58.6	57.4
Tetraallyl pentaerythritol	124-125	1.4595	0.9497	85.41	85.38		--	55.4	54.4
Diallyl ethylene glycol	35-37	1.4340	0.8340	41.50	41.42	0.97	--	57.8	57.0
Diallyl 1,3-butylene glycol	48-50	1.4330	0.8726	50.74	50.70	1.10	--	48.3	47.1
Diallyl dipropylene glycol	75-77	1.4380	0.9093	61.62	61.86	1.72	--	38.3	38.3

* At 1.5 mm.

TABLE V

Polymerization of tetra-allyl alpha-methyl glucoside at 97°*

Time elapsed, minutes	Viscosity in seconds	Viscosity in centistokes
0	2.6	2.7
60	3.2	3.0
120	8.5	8.0
146	17.7	16.8
160	27.8	26.4
182	67.8	64.4
189	93.6	88.6
196	133.6	126.5
204	231.9	219.5
208	∞**	∞**

*The reaction was conducted and the viscosity measured in a modified Ostwald pipette, through which oxygen was passed at a uniform rate.

**During this measurement the material gelled in the tube. In a control experiment in an atmosphere of CO₂ the material remained unchanged.

curious. Curves D and C show the effects of temperature at the addition of a catalyst on the polymerization of the glucoside. The gelation points for these curves are: A—270 min., B—3 min., C—185 min., D—170 min.

Fig. II. POLYMERIZATION OF POLYALLYL ETHERS

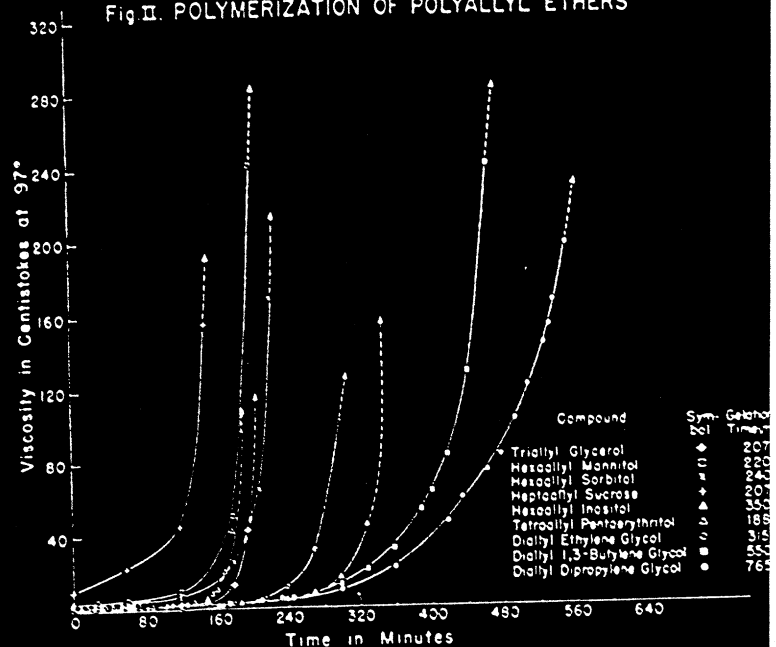
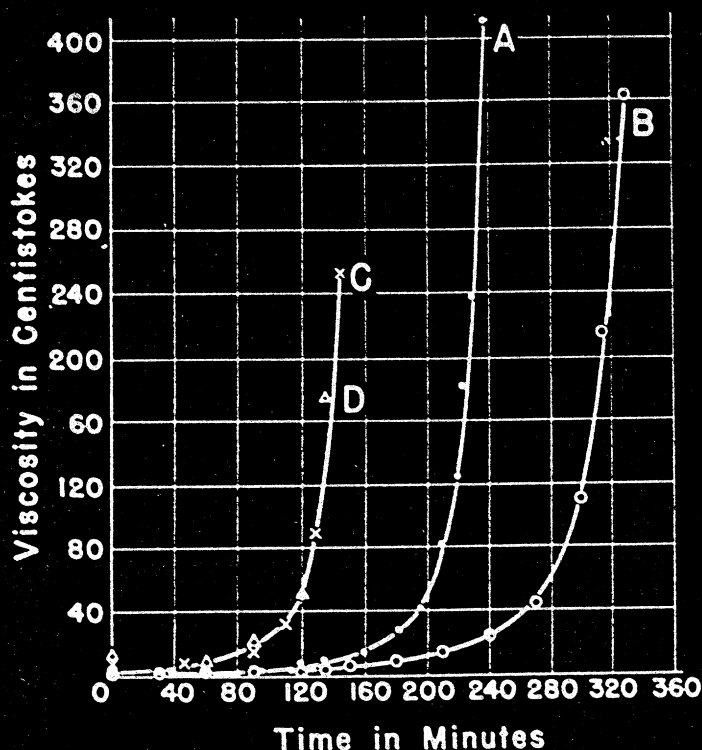


Fig.1

POLYMERIZATION OF ALLYL METHYL GLUCOSIDE (3.5 ALLYL GROUPS)

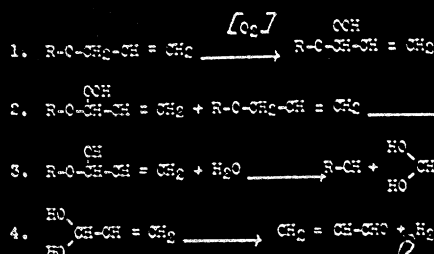
- A--At 97° oxygen-26l. per hour
 B-o-At 97° oxygen-7.5l. per hour
 C-x-At 97° oxygen-7.5l. per hr.+ Co naphthenate
 D-Δ-At 116.5° oxygen-7.5l. per hour



In general, the same type of polymerization occurred for all the compounds; however, as seen in Figure II, their rates of polymerization varied considerably. Compounds containing the greater number of allyl groups seemed to polymerize more readily, yet no clear relationship between gel points and the number of allyl groups was evident. By comparing the rates of gelation of diallyl ethylene glycol, diallyl 1,3-butylene glycol, and diallyl isopropylene glycol, the effect of structure on the rate of gelation is apparent.

Figures I and II show the general course of gelation and polymerization of various allyl ethers. In addition, the following phenomena were observed during polymerization.

1. An appreciable amount of oxygen actually combined with the compounds during polymerization. It was not a mere catalyst.



Sundralingam, in which the hydroperoxide oxidizes a double bond with the formation of an epoxy group. These two equations represent the application of Farmer's theory to our compounds. The hydroxy compound formed as a result of the second equation is a hemi-acetal, which would be readily hydrolyzed if a trace of water were present. From equations 3 and 4, it is evident that only a trace of water is necessary for complete hydrolysis of any amount of hemi-acetal formed, and according to Farmer's theory and our own observations water is formed during oxidations of this type. Inhibition of polymerization by alkalies can be readily explained on the basis of the theory advanced, since the hydroperoxides are readily hydrolyzed by alkalies.

The formation of epoxy groups in the above suggested scheme of oxidation and the well-known ease with which epoxy compounds polymerize lead us to suspect that this group plays an important role in the polymerization and cross-linkage of allyl ethers.

Thus the study of allyl ethers of simple carbohydrates may have a possible tentative explanation of their polymerization. Although from the theoretical interest, however, many allyl ethers of simple carbohydrates have possibilities for practical application.

All allyl ethers of simple carbohydrates are miscible with water and other and can be copolymerized. Besides, they are all soluble in allyl starch and can be copolymerized with the latter. As a result of their ability to polymerize to insoluble and infusible resins, the allyl ethers of polyhydric alcohols are useful as coatings, pregelating materials, and transparent adhesives. By various combinations of these materials, new and desirable properties can be attained. Thus a coating can be made harder or softer, or a combination can be chosen which will permit better penetration of the material into the body of wood or textile, or again a mixture can be chosen that will not go much beyond the surface of the material to be coated.

The data presented in this report are preliminary. Considerably more work remains to be done. The results to date, however, show clearly the possibilities of the substances described.

Postwar Exterior House Paint*

By S. WERTHAN*

Many pictures have been presented of postwar life in America, varying from a reversion to the conditions of the early thirties to a dazzling existence replete with synthetic food, clothes, home television and a plastic aeroplane to every family. The manufacturers' major interest, irrespective of the picture, is that his business will be affected. It is quite evident that whether or not some "dream houses" are built, there will be enough construction of the prewar type and there will be sufficient

cobalt naphthenate.

2. Peroxide was formed.
 3. Alkalies had an inhibiting effect on polymerization.
 4. Acrolein was formed during the reaction. The substance was isolated and identified as such.
- Any theory of polymerization advanced by us should also explain these phenomena.

If we accept the theory of Criegee, Pihl and Flygare (Ber., 72, 1799, 1939), and Farmer and Sundralingam (J. Chem. Soc., 1942, 121-139) on the autooxidation of olefinic compounds, there is a rather simple explanation for the addition of oxygen, the positive peroxide test, and the formation of acrolein. The following equations would represent the source of the reaction.

The first step shows formation of the hydroperoxide at the alpha-methylene carbon, which in this case should be especially reactive, since it is both adjacent to an ether oxygen and in alpha position to a double bond. The second step shows decomposition of the peroxide according to the scheme suggested by Farmer and

terior house paint shall I make?" Since we believe you may be interested in any information that may aid you in arriving at an answer, we have selected for this evening a discussion of a general investigation of postwar exterior house paint formulation our laboratory has under way.

The war restrictions on oil necessitated an abrupt digression from the long-established linseed oil vehicle for exterior house paints. As a result, consideration of oil modifications was forced upon the paint manufacturer, and in a relatively short period of time the industry had to change to vehicles containing high percentages of heavy bodied oil and of thinners. Although it is too early to draw definite conclusions as to the effects of the change in vehicle on the paint's durability, thus far, at least, we know of no serious or disastrous failures with the restricted oil type house paint, and our accelerated weathering and preliminary exterior test

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